# Mangroves as a Source of Alkalinity and Dissolved Carbon to the Coastal Ocean: A Case Study from the Everglades National Park, Florida

Gloria Maria Susanne Reithmaier<sup>1</sup>, David T. Ho<sup>2</sup>, Scott Johnston<sup>1</sup>, and Damien Troy Maher<sup>1</sup>

<sup>1</sup>Southern Cross University <sup>2</sup>University of Hawaii at Manoa

November 21, 2022

#### Abstract

Most research evaluating the potential of mangroves as a sink for atmospheric carbon has focused on carbon burial. However, the few studies that have quantified lateral exchange of carbon and alkalinity indicate that the dissolved carbon and alkalinity export may be several-fold more important than burial. This study aims to investigate rates and drivers of alkalinity, dissolved carbon and greenhouse gas fluxes of the mangrove-dominated Shark River estuary located in the Everglades National Park in Florida, USA. Time series and spatial surveys were conducted to assess total alkalinity (TAlk), organic alkalinity (OAlk), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), carbon dioxide (CO2), methane (CH4) and nitrous oxide (N2O). Dominant metabolic processes driving dissolved carbon and greenhouse gas dynamics varied along the estuarine salinity gradient. Dissolved carbon and greenhouse gas concentrations were strongly coupled to porewater input, which was examined using radon-222. Shark River was a source of CO2 (92 mmol/m2/d), CH4 (60  $\mu$ mol/m2/d) and N2O (2  $\mu$ mol/m2/d) to the atmosphere. Dissolved carbon export (DIC = 142 mmol/m2/d, DOC = 39 mmol/m2/d) was several-fold higher than burial (~28 mmol/m2/d) and represents an additional carbon sink. Furthermore, the estuary was a source of TAlk (97 mmol/m2/d, normalised to mangrove area) to the coastal ocean, potentially buffering coastal acidification. Organic alkalinity was also exported to the coastal ocean (1.9 mmol/m2/d, normalised to mangrove area). By integrating our results with previous studies, we argue that alkalinity, dissolved carbon and greenhouse gas fluxes should be considered in future blue carbon budgets.

# Mangroves as a Source of Alkalinity and Dissolved Carbon to the Coastal Ocean: A Case Study from the Everglades National Park, Florida

# 3 Gloria M. S. Reithmaier<sup>1</sup>, David T. Ho<sup>2</sup>, Scott G. Johnston<sup>1</sup>, Damien T. Maher<sup>1</sup>

- <sup>4</sup> <sup>1</sup>Southern Cross Geoscience, Southern Cross University, Lismore, New South Wales,
- 5 Australia.
- <sup>6</sup> <sup>2</sup>Department of Oceanography, University of Hawaii at Manoa, Honolulu, Hawaii 96822,
- 7 USĂ

Corresponding author: Gloria Reithmaier (g.reithmaier.10@student.scu.edu.au)

## 8 Key Points:

9 10	•	Estuarine carbon dynamics were driven by carbon remineralization, carbonate dissolution and porewater inputs
11 12	•	The mangrove-dominated estuary was a source of dissolved carbon and greenhouse gas emissions
13 14	•	Dissolved inorganic carbon export was severalfold higher than carbon burial and should be therefore integrated in blue carbon budgets

#### 15 Abstract

16 Most research evaluating the potential of mangroves as a sink for atmospheric carbon 17 has focused on carbon burial. However, the few studies that have quantified lateral exchange 18 of carbon and alkalinity indicate that the dissolved carbon and alkalinity export may be several-fold more important than burial. This study aims to investigate rates and drivers of 19 20 alkalinity, dissolved carbon and greenhouse gas fluxes of the mangrove-dominated Shark 21 River estuary located in the Everglades National Park in Florida, USA. Time series and 22 spatial surveys were conducted to assess total alkalinity (TAlk), organic alkalinity (OAlk), 23 dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), carbon dioxide ( $CO_2$ ), 24 methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O). Dominant metabolic processes driving dissolved 25 carbon and greenhouse gas dynamics varied along the estuarine salinity gradient. Dissolved 26 carbon and greenhouse gas concentrations were strongly coupled to porewater input, which was examined using radon-222. Shark River was a source of  $CO_2$  (92 mmol/m<sup>2</sup>/d), CH<sub>4</sub> (60 27 28  $\mu$ mol/m<sup>2</sup>/d) and N<sub>2</sub>O (2  $\mu$ mol/m<sup>2</sup>/d) to the atmosphere. Dissolved carbon export (DIC = 142) 29  $mmol/m^2/d$ , DOC = 39 mmol/m<sup>2</sup>/d) was several-fold higher than burial (~28 mmol/m<sup>2</sup>/d) and represents an additional carbon sink. Furthermore, the estuary was a source of TAlk (97 30 31  $mmol/m^2/d$ , normalised to mangrove area) to the coastal ocean, potentially buffering coastal 32 acidification. Organic alkalinity was also exported to the coastal ocean  $(1.9 \text{ mmol/m}^2/\text{d},$ 33 normalised to mangrove area). By integrating our results with previous studies, we argue that 34 alkalinity, dissolved carbon and greenhouse gas fluxes should be considered in future blue 35 carbon budgets.

#### 36 Plain language summary

37 Mangroves mitigate climate change by capturing carbon dioxide from the atmosphere. 38 Much research effort has gone into quantifying how much carbon is stored in mangrove soils. 39 However, less is known about the fate and magnitude of dissolved carbon fluxes. This study investigated dissolved carbon and greenhouse gas fluxes at the mangrove-dominated Shark 40 41 River located in the Everglades National Park in Florida, USA. To examine dissolved carbon 42 and greenhouse gas fluxes, we conducted temporal as well as spatial measurements. Our 43 results showed that dissolved carbon and greenhouse gases varied strongly within the study 44 area. Shark River was a source of greenhouse gas emissions to the atmosphere. However, 45 greenhouse gas fluxes were small compared to dissolved carbon export. Dissolved carbon 46 export was several-fold higher than carbon storage in soils. Therefore, more research is 47 required to evaluate the role of dissolved carbon export as a mangrove carbon sink.

# 48 **1 Introduction**

49 Mangroves play a disproportionately large role in the coastal carbon cycle. Carbon 50 storage in mangroves is exceptionally high compared to other forest ecosystems (Donato et al., 2011). Globally, mangrove soils store ~2.6 Pg C, which is equal to 9.5 Pg of  $CO_2$ 51 52 (Atwood et al., 2017) and the global carbon burial rate is estimated to be  $\sim 26$  Tg C/y 53 (Breithaupt et al., 2012). The blue carbon policy framework, which is increasingly used to 54 protect and restore coastal ecosystems, focuses on carbon burial of mangroves and other 55 vegetated coastal habitats. However, the carbon sink capacity of mangroves extends beyond 56 carbon burial (Maher et al., 2018). Part of the buried carbon is remineralized and exported as 57 dissolved carbon (Friesen et al., 2018; Maher et al., 2013a), which is largely unaccounted for 58 in current blue carbon budgets. Furthermore, carbon remineralization results in greenhouse 59 gas emissions, which partly offset carbon sequestration (Rosentreter et al., 2018b). To date, 60 there are very few studies that examine and integrate all aspects of mangrove carbon cycling 61 and their role in mitigating climate change, including carbon burial, carbon remineralization 62 and subsequent lateral export, as well as greenhouse gas emissions.

63 Whether mangroves act as source or sink for greenhouse gas emissions appears to 64 vary strongly between sites. A portion of the carbon fixed by mangroves is recycled as CO<sub>2</sub> 65 to the atmosphere. The global average CO<sub>2</sub> emission by mangroves is estimated to be  $34 \pm 5$ Tg C/y (Rosentreter et al., 2018a), which is slightly higher than estimated global carbon 66 67 burial rates in mangroves (Breithaupt et al., 2012). Compared to CO<sub>2</sub>, total methane (CH<sub>4</sub>) emissions (water and sediment fluxes) by mangroves are thought to be small  $(0.273 \pm 0.053)$ 68 69 Tg C/y) (Rosentreter et al., 2018b). Nonetheless, accounting for CH<sub>4</sub> emissions is important 70 due to CH<sub>4</sub> having a higher global warming potential than CO<sub>2</sub> (IPCC, 2014). Nitrous oxide 71 (N<sub>2</sub>O), which is an even stronger greenhouse gas than CH<sub>4</sub>, is believed to be emitted at rates 72 of 0.01 - 0.09 Tg N/y by mangroves globally (Murray et al., 2015), but pristine mangroves 73 can also act as N<sub>2</sub>O sink (Maher et al., 2016).

74 In contrast to greenhouse gas emissions, which offset carbon sequestration, the lateral 75 export of remineralized carbon may enhance the carbon sink associated with mangroves. In 76 mangroves, carbon, which is mainly remineralized via sulfate reduction and aerobic 77 respiration, is predominantly exported as dissolved inorganic carbon (DIC =  $CO_2 + HCO_3^- +$ 78  $CO_3^{2-}$ ) and to a lesser extent as dissolved organic carbon (DOC) (Faber et al., 2014; Ho et al., 79 2017; Maher et al., 2013a; Taillardat et al., 2018). The global DOC exported by mangroves is 80 estimated to be  $24 \pm 21$  Tg C/y (Bouillon et al., 2008). Despite the important role of DIC, 81 current global estimates  $(43 \pm 12 \text{ Tg C/y})$  for mangrove DIC export, which are twice as high 82 as global mangrove carbon burial rates, are derived from only six Australian mangrove creeks 83 (Sippo et al., 2016). This limited spatial coverage of mangrove DIC export estimates 84 represents a major gap in developing a holistic understanding of global mangrove carbon 85 cycling. During export to the coastal ocean, DIC partly outgasses as CO<sub>2</sub> to the atmosphere, whereas carbonate alkalinity (HCO<sub>3</sub><sup>-</sup> + CO<sub>3</sub><sup>2-</sup>) effectively remains dissolved in the ocean with 86 an oceanic residence time of ~ 100,000 years (Emerson & Hedges, 2008). In addition to 87 88 being a long-term carbon sink, total alkalinity (TAlk) exported to coastal waters may help 89 buffer acidification in near-shore coastal waters (Faber et al., 2014; Sippo et al., 2016).

An understudied component of TAlk is organic alkalinity (OAlk), which contributes to TAlk when organic substances are present. Previous studies have found significant contributions of OAlk in rivers (Hunt et al., 2011), estuaries (Cai et al., 1998; Tishchenko et al., 2006), coastal waters (Hernández-Ayon et al., 2007; Hunt et al., 2011; Ko et al., 2016), and the open ocean (Fong & Dickson, 2019). In the coastal and marine environment, OAlk is produced by photosynthesis, for instance by phytoplankton (Kim & Lee, 2009) and algae 96 (Hernández-Ayon et al., 2007), or by carbon remineralization (Lukawska-Matuszewska et al.,

2018). To our knowledge, research investigating OAlk in mangroves is limited to one study,
which reported OAlk values up to 47 µmol/kg for seven point measurements (Yang et al.,
2015).

100 This study aims to update the mangrove carbon budget, with a specific focus on 101 aquatic exports, by examining alkalinity, dissolved carbon and greenhouse gas fluxes at the 102 mangrove-dominate Shark River located in the Everglades National Park Florida. We 103 quantified estuarine fluxes and evaluated their underlying drivers, such as carbon 104 mineralization and porewater inputs, by applying contrasting spatial surveys and time series 105 approaches. Furthermore, we present the first study analysing the dynamics and relevance of 106 OAlk in mangrove-dominated estuaries.

#### 107 2 Methods

108 2.1 Study site

109 Shark River is located in Everglades National Park, South Florida (Figure 1) and flows into the Gulf of Mexico. The subtropical climate of South Florida is characterised by a 110 111 dry season from November to April (average monthly rainfall 54 mm) and a wet season from 112 May to October (average monthly rainfall 189 mm). Average monthly minimum and maximum temperatures range between 12 and 34 °C (Southeast Regional Climate Center, 113 114 http://www.sercc.com). The area is subject to a semi-diurnal tidal regime, with a mean tidal 115 amplitude of 0.5 - 1 m. Shark River is surrounded by a large mangrove forest (144,447 ha), which has a net ecosystem production (NEP) of  $1170 \pm 127$  gC/m<sup>2</sup>/y (Barr et al., 2010). The 116 mangrove forest is dominated by Rhizophora mangle, Avicennia germinans, Laguncularia 117 118 racemose, and Conocarpus erectus (Chen & Twilley, 1999). The freshwater reaches of the 119 low-lying Shark River Slough are comprised of freshwater marshes, which are dominated by 120 Cladium jamaicense (Olmsted & Armentano, 1997). The underlying geology of the study 121 area is characterized by a flat carbonate platform formed during the late Mesozoic and the 122 Cenozoic (Petuch & Roberts, 2007).





Figure 1. Map presenting mangrove cover (green), time series stations (red crosses) at Shark River within
 Everglades National Park (black border). Photographs show the dense mangrove forest fringing Shark River.

126 2.2 Sample collection and analysis

Two longitudinal surveys (SV1, SV2; ~15 km) and two 30 h time series were conducted at Shark River between the 21st and 26th November 2018 (Figure 1). The time series stations are named according to the water quality stations managed by the National Park Service (NPS). The upstream time series station is adjacent to Gunboat Island (GI) (25.3782, -81.0295) and the downstream time series station is towards the mouth of Shark River (SR) (25.3541, -81.1005). Surface water was analysed by automated, continuous 133 underway measurements as well as by discrete measurements on an hourly basis during the 134 time series measurements and approximately every two salinity units during the spatial 135 surveys.

136 Surface water from a water depth of approximately 0.5 m was continuously pumped 137 into the on-board measurement setup. Salinity ( $\pm 0.01$ ) and water temperature ( $\pm 0.002$  °C) 138 were measured using a thermosalinograph (SBE 45 MicroTSG). A ion-sensitive field-effect 139 transistor (Honeywell Durafet II) was used to determine pH ( $\pm 0.005$ ) as described by Martz et al. (2010). Dissolved oxygen (DO, ±0.06%) was measured with an oxygen optode 140 141 (Aanderaa 3835) calibrated against Winkler titration. Fluorescent dissolved organic matter 142 (fDOM) was analysed with a fluorometer on a multiparameter Sonde (YSI EXO2), which has 143 a detection limit of 0.07 ppb QSE. Dissolved inorganic carbon samples were acidified in a 144 DIC analyser as described by Friederich et al. (2002), to transfer all carbonate species into 145 CO<sub>2</sub>, and subsequently analysed with a non-dispersive infrared absorption (NDIR) detector 146 (LI-COR LI-7000), with a precision better than 0.1%.

Continuous CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub> (1 min intervals) and radon-222 (<sup>222</sup>Rn, min intervals) 147 148 concentrations were measured via a showerhead equilibrator coupled to gas analysers (Santos 149 et al., 2012). Concentrations of CO<sub>2</sub> and CH<sub>4</sub> were analysed during SV1 and time series at GI with a mobile gas concentration analyser (Picarro GasScouter<sup>TM</sup> G4301) with a raw 150 151 precession of 0.4 ppm and 3 ppb, respectively. Nitrous oxide concentrations ( $\pm 2$  ppb), as well 152 as  $CO_2$  (±10 ppm) and  $CH_4$  (±10 ppb) concentrations for SV2 and SR time series, were analysed with by cavity ring-down spectroscopy (Picarro G2308) (Maher et al., 2013b). A 153 radon detector (Durridge RAD7) was used to measure <sup>222</sup>Rn (Burnett et al., 2001). 154 155 Equilibration times of all gases were corrected according to Webb et al. (2016).

156 For TAlk and OAlk analysis, samples were filtered with 0.7 µm GFF filters and 157 measured within one day, using a titrator (Metrohm 888 Titrando with Tiamo light), which 158 has a precision better than 5 µM. Deviations and drifts in the acid concentration (0.05 M 159 hydrochloric acid) were accounted for, using certified reference materials (CRM batch 175 and CRM batch 178) according to Dickson (2010). The method developed by Cai et al. 160 161 (1998) was adapted for OAlk determination. Following the first Gran titration, which 162 determines TAlk, samples were purged with high purity nitrogen for five minutes to remove 163 the  $CO_2$  and then back-titrated to the original pH with sodium hydroxide (0.05 M). 164 Subsequently, a second Gran titration was undertaken on the sample, which determines the non-carbonate alkalinity. To calculate OAlk, results were corrected for borate alkalinity, 165 166 which was calculated from TAlk, pH, temperature and salinity using CO2SYS (Lewis & 167 Wallace, 1998). For DOC analysis, samples were filtered with 0.7 µm GFF filters, preserved 168 with phosphoric acid and analysed with a total organic carbon analyser (Shimadzu TOC-L 169 CSH/CSN), which has a precision better than 2%.

170 2.3 Calculations

Estuarine input concentrations of dissolved parameters were estimated by a linear mixing model (Kaul & Froelich, 1984). Theoretical linear mixing lines were aligned to observed values at lowest and highest salinities, representing freshwater and seawater endmembers, and the deviation between conservative mixing values and measured values was determined. The deviation values were integrated over the entire survey and divided by the salinity range to get input concentrations. In order to examine lateral export values, the estuarine input concentration was multiplied by the water volume (9400000 m<sup>3</sup>) and divided 178 by the water residence time (4.88 d), which was calculated by applying an equation 179 developed for Shark River by Ho et al. (2016):

180 
$$\tau = 3.678 + 26.718e^{-0.367Q}$$

(1)

(2)

181 Where  $\tau$  is the residence time and Q is the tidally filtered discharge at Gunboat Island 182 (U.S. Geological Survey, 2018). Rates were normalized to the associated tidally inundated 183 area (15.9 km<sup>2</sup>) for Shark River (Ho et al., 2017) to scale fluxes to mangrove area for 184 comparison with previous studies. Due to the high uncertainty about this area, ranges for 185 areal fluxes were determined by using half and twice the size of the inundated mangrove area.

186 In addition to the Lagrangian approach, an Eulerian approach was applied to quantify 187 lateral fluxes. Lateral TAlk, DIC and DOC fluxes were calculated by multiplying 188 concentrations, which were sampled during time series measurements, with discharge at 15-189 minute intervals. To attain higher temporal resolution for TAlk, OAlk and DOC flux rates, 190 TAlk was calculated using CO2SYS from high-resolution measurements of DIC and pH 191 (Pierrot et al., 2009), and DOC as well as OAlk were calculated from fDOM using linear 192 relationships (see discussion). Concentrations were averaged for each time step. Discharge 193 values were retrieved from the U.S. Geological Survey station at Gunboat Island (U.S. 194 Geological Survey, 2018). Start and end time were adjusted to balance the water volumes and 195 included two complete tidal cycles. Positive values indicate fluxes directed towards the 196 ocean. To get areal rates (i.e.,  $mmol/m^2/d$ ), total fluxes have been scaled to the estimated inundated area between the time series stations (8.7 km<sup>2</sup>), whose boundaries were, due to the 197 198 lack of a high-resolution DEM, estimated to be halfway to the next watercourse. Similar to 199 the Eulerian approach, uncertainties on the areal fluxes were accounted for by halving and 200 doubling inundation area.

201 Concentrations of  $CO_2$ ,  $CH_4$  and  $N_2O$  were corrected for water vapour removal and 202 converted to partial pressure according to the methods detailed in Pierrot et al. (2009). Air-203 water gas fluxes of  $O_2$ ,  $CO_2$ ,  $CH_4$  and  $N_2O$  were determined, as product of the gas transfer 204 velocity, the solubility coefficient and the difference in the air-water partial pressure:

205 
$$F_{CO2} = k_{CO2} K_0 (pCO_{2(water)} - pCO_{2(air)})$$

where  $F_{CO2}$  is the CO<sub>2</sub> flux (mmol/m<sup>2</sup>/d),  $k_{CO2}$  is the gas transfer velocity,  $K_0$  is the 206 solubility coefficient,  $pCO_{2(water)}$  is the partial pressure of  $CO_2$  in water and  $pCO_{2(air)}$  is the 207 208 partial pressure of  $CO_2$  in air. The same calculation was applied to determine oxygen ( $O_2$ ). 209 CH<sub>4</sub> and N<sub>2</sub>O air-water fluxes. The solubility coefficients were calculated as a function of salinity and temperature for O<sub>2</sub> (Benson & Krause, 1984), CO<sub>2</sub> (Weiss, 1974), CH<sub>4</sub> 210 211 (Wiesenburg & Guinasso Jr, 1979) and N<sub>2</sub>O (Weiss & Price, 1980). Atmospheric partial 212 pressures of 412 µatm for CO<sub>2</sub>, 1.8 µatm for CH<sub>4</sub> and 0.33 µatm for N<sub>2</sub>O were used. 213 According to the convention, positive values presenting a flux towards the atmosphere. The 214 gas transfer velocity was calculated:

215 
$$k_{CO2} = k(600) (Sc_{CO2}/600)^{-0.5}$$
 (3)

216 where k(600) is the gas transfer velocity normalized to a Schmidt number of 600 and 217 Sc<sub>C02</sub> is the Schmidt number, which was calculated as function of temperature and salinity 218 assuming a linear dependence of the Schmidt number on salinity (Wanninkhof, 2014). 219 Integrating wind speed, current velocity and water depth, k(600) was calculated according to 220 Ho et al. (2016), who conducted deliberate gas tracer experiments in the Shark River to 221 derive an empirical equation for k(600) determination: 222  $k(600) = 0.77v^{0.5}h^{-0.5} + 0.266u_{10}^{2}$ 

(4)

where v is the current velocity, h is the mean depth of Shark River (2.8 m) (Ho et al., 224 2014) and  $u_{10}$  is the wind speed at 10 m height, which was recorded on site with a weather 225 station (ATMOS 41). Gas fluxes were interpolated to the water area of the entire Shark River 226 (2.2 km<sup>2</sup>) and the area between the time series stations (0.9 km<sup>2</sup>), using the spatial analyst 227 tool of ArcGIS 10.6.1 (Maher & Eyre, 2012).

Statistical analysis was conducted in SigmaPlot 14.0. The Pearson correlation coefficients (*r*) were determined for alkalinity, dissolved carbon, greenhouse gases and the explanatory variables (salinity, <sup>222</sup>Rn and DO) to evaluate underlying drivers. The probability levels are presented as \* if p < 0.05, \*\* if p < 0.01 and \*\*\* if p < 0.001. For the linear regressions between OAlk, DOC and fDOM, coefficients of determination ( $R^2$ ) have been reported.

#### 234 **3 Results**

235 The spatial variations in alkalinity, dissolved carbon and greenhouse gases along the 236 Shark River show clear estuarine trends (Figure 2). Within the mangrove zone, TAlk, DIC 237 and CO<sub>2</sub> peak at brackish waters, whereas DOC is highest at upstream freshwater sites. In 238 comparison, CH<sub>4</sub> and N<sub>2</sub>O show less distinct patterns, but decrease, like all parameters, 239 towards the Gulf of Mexico. It has to be noted that Shark River flows through a very flat 240 terrain and is highly connected with other streams and creeks.

81°6'0"W 81°4'0"W 81°2'0"W 81°0'0"W 80°58'0"W 81°6'0"W 81°4'0"W 81°2'0"W 81°0'0"W 80°58'0"W





Figure 2. Maps of Shark River showing total alkalinity (TAlk, a), dissolved inorganic carbon (DIC, b), 243 dissolved organic carbon (DOC, c) recorded during the first survey (SV1) and the partial pressure of carbon 244 dioxide ( $pCO_2$ , d), methane ( $pCH_4$ , e) and nitrous oxide ( $pN_2O$ , f) recorded during the second survey (SV2).

245 Ranges and trends of all measured parameters varied little between the two spatial 246 surveys (Figure 3). Dissolved oxygen saturation (36 - 82%) and pH (7.4 - 7.8) showed a 247 concave down pattern along the salinity gradient, which ranged from 0.7 to 29. The average 248 water temperature during SV1 (25.9 °C) was slightly higher than during SV2 (25.2 °C). Radon declined from 5014 dpm/m<sup>3</sup> in brackish waters to 329 dpm/m<sup>3</sup> towards the river 249 mouth. Similar to  $^{222}$ Rn, pCO<sub>2</sub> (1643 – 5873 µatm) and pCH<sub>4</sub> (46 – 82 µatm, 53 – 105 nM) 250 increased at intermediate salinities. In contrast, N<sub>2</sub>O ( $0.36 - 0.49 \mu atm$ , 7 - 12 nM) decreased 251 slightly towards higher salinity. Both, TAlk and DIC showed similar concentrations and 252 253 trends ranging from 2913 to 4255 µmol/kg and from 2753 to 4277 µmol/kg, respectively.

- 254 Concentrations of OAlk  $(0 - 81 \mu mol/kg)$  decreased almost linearly with increasing salinity,
- 255 while DOC (604 – 1422 µmol/L) and fDOM (39 – 161 ppb) were non-conservative. During
- 256 SV2 wind speed varied between 0.81 and 1.88 m/s.



257 258 Figure 3. Biochemical parameters were measured during two spatial surveys along the Shark River. Oxygen 259 (DO, a), radon-222 (<sup>222</sup>Rn, b), temperature (c), carbon dioxide (pCO<sub>2</sub>, d), methane (pCH<sub>4</sub>, e), nitrous oxide 260 (pN<sub>2</sub>O, f), total alkalinity (TAlk, g), dissolved inorganic carbon (DIC, h), pH (i), organic alkalinity (OAlk, j), 261 dissolved organic carbon (DOC, k) and fluorescent dissolved organic matter (fDOM, l) are plotted against 262 salinity. Dashed lines represent linear mixing curves.

263

Positive deviations from linear mixing curves indicate inputs of alkalinity and 264 dissolved carbon (Figure 3). Input concentrations of TAlk (527 µmol/kg) and DIC (664 265 µmol/kg) were high compared to DOC (100 µmol/L) and fDOM (19 ppb). At the brackish section, the estuary was a sink for OAlk, but turned into an OAlk source at salinities above 10 266 267 (5 µmol/kg). The greenhouse gases CO<sub>2</sub> and CH<sub>4</sub> showed a distinct non-conservative behaviour, suggesting a source within the estuary, whereas N<sub>2</sub>O exhibited an alternating 268 269 source-sink behaviour.

270 The two time series stations were exposed to contrasting salinity ranges, with values 271 ranging from 3 to 22 at GI and from 26 to 29 at SR (Figure 4). The upstream site GI 272 experienced freshwater DO input during low tide and seawater DO input during high tide (31 273 - 41% saturation), and pH (7.4 - 7.6) was negatively correlated with salinity with small peaks 274 at high tide. Being mainly controlled by oceanic influences, DO (53% - 85% saturation) and 275 pH (7.6 – 7.9) changed simultaneously with salinity at SR. Water temperatures were similar 276 for both time series stations, averaging 24.8 °C. At the GI site,  $^{222}$ Rn reached twofold higher 277 values (5648 – 9969 dpm/m<sub>3</sub>) compared to the SR site (1437 – 6515 dpm/m<sup>3</sup>). During the 278 times series at GI, discharge ranged from -186 to 189 m<sup>3</sup>/s and during time series at SR from 279 -239 to 218 m<sup>3</sup>/s.



280

Figure 4. Biochemical parameters were measured at upstream (GI) and downstream (SR) time series stations at Shark River. Oxygen (DO, a), radon-222 ( $^{222}$ Rn, b), temperature (c), carbon dioxide (pCO<sub>2</sub>, d), methane (pCH<sub>4</sub>, e), nitrous oxide (pN<sub>2</sub>O, f), total alkalinity (TAlk, g), dissolved inorganic carbon (DIC, h), pH (i), organic alkalinity (OAlk, j), dissolved organic carbon (DOC, k) and fluorescent dissolved organic matter (fDOM, l) are plotted against salinity.

At both stations, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, TAlk, DIC, DOC and fDOM were inversely related 286 to salinity (Figure 4). During time series at GI,  $pCO_2$  (3976 – 6240 µatm) and  $pCH_4$  (43 – 100 287 288  $\mu$  atm, 56 – 134 nM) were much higher compared to pCO<sub>2</sub> (1257 – 2272  $\mu$  atm) and pCH<sub>4</sub> (12 -34 µatm, 14 – 39 nM) at SR. In contrast, N<sub>2</sub>O reached almost similar values at both stations 289 290  $(0.31 - 0.42 \mu atm, 7 - 10 nM)$ . At GI, TAlk ranged from  $3704 - 4368 \mu mol/kg$  and at SR 291 from 2832 – 3315 µmol/kg. Concentrations of DIC ranged from 3702 – 4348 µmol/kg at GI 292 and from 2765 – 3214 µmol/kg at SR. Due to equipment failure, OAlk data are only available for the GI site (35 - 61 µmol/kg). Concentrations of DOC were two times and fDOM was 293 294 three times higher at GI ( $934 - 1458 \mu mol/L$ , 91 - 159 ppb) compared to SR (504 - 825295  $\mu$ mol/L, 35 – 59 ppb).

Comparing time series with the spatial surveys, DO, TAlk, DIC and DOC concentrations and trends were similar, whereas  $^{222}$ Rn and the greenhouse gases showed different trends. Unlike the spatial surveys,  $^{222}$ Rn, CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O followed a hysteresis pattern during the time series measurements, reaching higher values at a given salinity during flood tide at both stations. The hysteresis was less developed for CO<sub>2</sub> than for CH<sub>4</sub>, N<sub>2</sub>O and  $^{222}$ Rn. During time series,  $^{222}$ Rn values were at least twice higher than during the spatial surveys.

303 Shark River was a source for all studied greenhouse gases and a sink for DO (Table 304 1). Referring to the water area  $(0.94 \text{ km}^2)$  between the time series stations, DO uptake by the 305 river (-2.1 x 10<sup>5</sup> mol/d) was threefold higher than CO<sub>2</sub> emissions (6.4 x 10<sup>4</sup> mol/d). In 306 comparison, CH<sub>4</sub> emissions (53 mol/d) played only a minor role and N<sub>2</sub>O emissions (1 mol/d) 307 were negligible.

308 During the time series measurements, dissolved carbon and alkalinity were exported 309 to the ocean (Table 1). The fluxes at upstream GI were considerably smaller, constituting only 4 – 15% of the fluxes at downstream SR. At GI, DIC and DOC fluxes were comparable, 310 311 whereas at SR the DIC (76%) was the major dissolved carbon export. Fluxes of DIC and TAlk were similar (1 x  $10^6$  mol/d) at SR, but at GI DIC (5 x  $10^4$  mol/d) was lower than TAlk 312  $(1 \times 10^5 \text{ mol/d})$ . At both sites, the OAlk flux accounted for 2% of the TAlk flux and 5% of the 313 314 DOC flux. The difference between the fluxes at both time series stations is equal to the input 315 by the mangrove-dominated area in between. The estuarine input was  $1 \times 10^6$  mol/d of DIC. 8 x  $10^5$  mol/d of TAlk, 3 x  $10^5$  mol/d of DOC and 2 x  $10^4$  mol/d of OAlk. The DIC input was 316 317 13 times higher than the CO<sub>2</sub> emission and 78% of the dissolved carbon input.

Fluxes estimated with the Lagrangian approach for the entire Shark River, were similar to the fluxes acquired during the time series (Table 1). Areal rates were slightly smaller for the Lagrangian approach, which included the entire estuary, than for the Eulerian approach, which covered the mangrove-dominated sections of the estuary.

322	Table 1. Air-water fluxes are shown for entire Shark River and the mangrove-dominated area between time
323	series stations. Lateral fluxes are presented for at the upstream station (GI), the downstream station (SR) and the
324	input by the mangrove-dominated area between the time series stations using the Eulerian and Lagrangian
325	approach. Uncertainty bands for areal rates are shown in brackets.

Air-water	DO flux	CO <sub>2</sub> flux	CH4 flux	N <sub>2</sub> O flux		
Shark River (mol/d) Shark River (mmol/m <sup>2</sup> /d)	$-6.3 \times 10^5$ -285	$2.0 \times 10^5$ 92	136 0.06	3.6 0.002		
Mangrove area (mol/d) Mangrove area (mmol/m <sup>2</sup> /d)	-2.1 x 10 <sup>3</sup> -222	6.4 x 10 <sup>+</sup> 68	53 0.06	1.0 0.001		
Lateral	DIC flux	TAlk flux	DOC flux	OAlk flux		
GI station (mol/d) SR station (mol/d) Eulerian (mol/d) Eulerian (mmol/m <sup>2</sup> /d) Lagrangian (mol/d) Lagrangian (mmol/m <sup>2</sup> /d)	$5.5 \times 10^{4}$ $1.3 \times 10^{6}$ $1.2 \times 10^{6}$ $142 (71 - 284)$ $1.3 \times 10^{6}$ $80 (40 - 161)$	$\begin{array}{c} 1.3 \ \text{x} \ 10^5 \\ 9.7 \ \text{x} \ 10^5 \\ 8.4 \ \text{x} \ 10^5 \\ 97 \ (48 - 193) \\ 1.0 \ \text{x} \ 10^6 \\ 64 \ (32 - 128) \end{array}$	$5.5 \times 10^{4}  4.0 \times 10^{5}  3.4 \times 10^{5}  39 (20 - 79)  1.9 \times 10^{5}  12 (4 - 24)$	$2.9 \times 10^{3}$ $2.0 \times 10^{4}$ $1.7 \times 10^{4}$ 1.9 (1.0 - 3.9) $9.6 \times 10^{3}$ 0.6 (0.3 - 1.2)		

326 Pearson's correlation coefficients between alkalinity, dissolved carbon, greenhouse gases and the explanatory variables salinity, <sup>222</sup>Rn and DO provide insights into underlying 327 drivers of estuarine processes (Table 2). Salinity was a good predictor (negatively correlated) 328 329 for most parameters. Correlations between CH<sub>4</sub>, N<sub>2</sub>O and salinity were less evident during 330 the spatial surveys and GI, respectively. During the spatial surveys, the natural groundwater tracer <sup>222</sup>Rn was highly correlated ( $r \ge 0.78$ ) with all parameters. However, the relationship 331 between <sup>222</sup>Rn and measured parameters was not as strong during the time series 332 333 measurements, except for  $CH_4$  (r > 0.70). Oxygen (a proxy for aerobic metabolism) was 334 negatively correlated to parameters measured during the spatial surveys and the SR time 335 series. In contrast, DOC and OAlk had weaker correlations with DO.

336	Table 2. Pearson correlations between dissolved carbon, alkalinity, greenhouse gases and the explanatory
337	variables for upstream (GI) and downstream (SR) time series and both spatial surveys (SV).

_	Variables	DIC	DOC	TAlk	OAlk	CO <sub>2</sub>	CH <sub>4</sub>	$N_2O$
SV	Salinity	-0.73***	-0.96***	-0.71***	-0.92***	-0.66***	-0.23***	-0.81***
	<sup>222</sup> Rn	0.97***	0.92***	0.97***	0.81**	NA	NA	0.78***
	DO	-0.90***	-0.50*	-0.84***	-0.30	-0.96***	-0.70***	-0.38***
GI	Salinity	-0.89***	-0.94***	-0.86***	-0.79***	-0.90***	-0.41***	0.05
	<sup>222</sup> Rn	0.05	0.23	0.07	0.04	0.34***	0.70***	0.56***
	DO	-0.64***	-0.37	-0.49*	-0.14	-0.63***	0.17***	0.46***
SR	Salinity	-0.96***	-0.48**	-0.74***	NA	-0.87***	-0.65***	-0.68***
	<sup>222</sup> Rn	0.52***	0.12	0.55**	NA	0.63***	0.80***	0.53***
	DO	-0.94***	-0.44*	-0.89***	NA	-0.97***	-0.84***	-0.82***

#### 338 4 Discussion

339 4.1 Relevance and proxies of organic alkalinity

340 Despite the potential relevance of OAlk, many studies do not directly measure but calculate OAlk (Hammer et al., 2017; Hernández-Ayon et al., 2007; Kim & Lee, 2009; 341 342 Kuliński et al., 2014; Lukawska-Matuszewska et al., 2018). Organic alkalinity is often 343 estimated as the difference between observed and calculated TAlk, which is determined by 344 the carbonate system and can therefore be calculated from pH, DIC or pCO<sub>2</sub>. Testing all 345 available dissociation constants in CO2SYS, constants derived from Millero (2010), which were determined for estuarine waters, were found to be the best fit for OAlk calculations at 346 Shark River. However, there were substantial discrepancies between calculated and measured 347 348 OAlk (Figure 5a). Along the salinity gradient, the slopes of salinity versus calculated OAlk 349 were higher than for salinity versus measured OAlk, resulting in overestimation at low and underestimation at high salinities (Figure 5b). This salinity dependant discrepancy between 350 measured and calculated OAlk suggests that the published dissociation constants may not be 351 352 applicable for Shark River, where measured TAlk and DIC concentrations were twice as high 353 than concentrations of seawater, which was used for determining dissociation constants (Millero, 2010). It can be concluded that in estuarine systems, either site specific dissociation 354 355 constants should be developed and verified or OAlk should be measured rather than 356 calculated.



Figure 5. Organic alkalinity was calculated (OAlk<sub>calculated</sub>) as the difference between measured total alkalinity
 and total alkalinity calculated from dissolved inorganic carbon and pH or dissolved inorganic carbon and the

partial pressure of carbon dioxide. Calculated values differed considerably from measured organic alkalinity
 (OAlk<sub>measured</sub>) (a). Calculations lead to overestimations at low and underestimations at high salinity (b).

362 An alternative approach to either laborious OAlk measurements or OAlk calculations is the use of proxies. Exploring the suitability of potential proxies, we found DOC ( $R^2 = 0.78$ ) 363 to be a good predictor for OAlk (Figure 6). Previous studies similarly suggested a close 364 365 relationship between OAlk and DOC (Kim & Lee, 2009; Koeve & Oschlies, 2012; Kuliński 366 et al., 2014; Ulfsbo et al., 2015). Conducting spike experiments with artificial seawater, 367 Hammer et al. (2017) found linear relationships between DOC and OAlk, with different slopes for humic (0.1) and fulvic (0.08) substances. The slope at Shark River (0.06) suggests 368 369 that fulvic substances might contribute more to OAlk than humic substances at this site. 370 Using water of two rivers, an organic matter enrichment experiment showed very similar 371 OAlk-DOC slopes (0.06 and 0.07), but unlike our study, a positive intercept was found 372 (>148) (Kuliński et al., 2014). Compared to other studies, which reported contributions of up 373 to 100% (Cai et al., 1998; Hunt et al., 2011; Kuliński et al., 2014), OAlk at Shark River 374 accounted only for a small share of DOC (4%). The negative intercept for OAlk and DOC 375 regressions demonstrate that for DOC concentrations < 600 µmol/L no OAlk was present, 376 suggesting that all acid functional groups were protonated. The low OAlk contribution to 377 DOC compared to other studies might be due to differences in temperature, salinity, pH and 378 organic compound composition (thus different pk<sub>a</sub> values), which affect the acid-base 379 behaviour of organic matter (Cai et al., 1998).

380 A cost and time efficient alternative to DOC measurements is the use of fDOM 381 sensors, which are increasingly used to monitor DOC at a high temporal resolution (Baker & 382 Spencer, 2004; Suryaputra et al., 2015). In line with previous findings, the present study showed that fDOM was a very good proxy for DOC ( $R^2 = 0.98$ ) over a broad salinity range 383 (Figure 6). Hence, similar to DOC, fDOM was also a good predictor for OAlk ( $R^2 = 0.74$ ), 384 385 thus suggesting that fDOM sensors may be a useful alternative technique for high-resolution 386 OAlk monitoring, but more research needs to be undertaken to confirm the use of fDOM as 387 an OAlk proxy.



**Figure 6.** Organic alkalinity (OAlk) was correlated with dissolved organic carbon (DOC, a) and fluorescent dissolved organic matter (fDOM, b). Fluorescent dissolved organic matter was a very good proxy for dissolved organic carbon (c). All linear regressions had probability levels of p < 0.001, except for fDOM versus DOC at SR (p = 0.004).

393 Concentrations of OAlk at Shark River  $(0 - 81 \mu mol/kg)$  accounted for ~1% of TAlk 394 and were comparable to literature values for mangroves and other vegetated coastal habitats. 395 Yang et al. (2015) calculated OAlk for seven mangrove sites in the Gulf of Mexico, Florida, 396 reporting values between -16 and 47 µmol/kg for salinities higher than 23. Measuring OAlk 397 along salinity gradients of saltmarsh dominated rivers in Georgia, Cai et al. (1998) found 398 OAlk concentrations reaching from 8 to 112 µmol/L. At a Ramsar site in San Quintín Bay, 399 Mexico, which is vegetated by seagrasses and saltmarshes, OAlk concentrations ranged between 20 – 75 µmol/kg (Hernández-Ayon et al., 2007). The small share of OAlk to TAlk 400 401 (1%) compared to previous studies (up to 23%) (Cai et al., 1998), is attributed to the higher 402 overall TAlk concentrations (up to 4368 µmol/kg) in Shark River.

403 Along the salinity gradient, OAlk was removed during early stages of mixing at 404 upstream sites, whereas the mangrove-dominated area represented a net source for OAlk (5 umol/L). During estuarine mixing, OAlk can be removed by protonation of humic acids (Cai 405 406 et al., 1998) and organic matter removal driven by photodegradation (Moran et al., 2000), 407 remineralisation (Maher & Eyre, 2010), or flocculation (Sholkovitz et al., 1978). At the mangrove-dominated area between the time series stations, OAlk input exceeded the 408 409 removal, resulting in a lateral export of OAlk towards the ocean, which accounted for 2% of 410 the TAlk export. However, even small OAlk concentrations can have a large effect on the pH. Calculations showed that the pH of Shark River would be up to 0.3 units lower without the 411 412 presence of OAlk. Even though it represents only a small proportion of the TAlk pool and 413 fluxes, OAlk may substantially buffer the pH of estuarine and coastal waters. However, how 414 this OAlk affects buffering capacity and pH of estuarine and coastal waters remains 415 challenging to constrain, due to the complex mixture of organic compounds contributing to 416 the OAlk pool with varying pK<sub>a</sub> and biogeochemical reactivity (Hu, 2020). Nonetheless, our 417 results suggest that further investigations on OAlk inputs from mangroves is warranted.

## 418 4.2 Drivers of alkalinity, dissolved carbon and greenhouse gas dynamics

Despite the comprehensive data acquisition during the measurements presented here, our measurements were undertaken over a short period. Alkalinity, dissolved carbon, and greenhouse gases are known to vary between seasons (Koné & Borges, 2008; Volta et al., 2018) and over spring neap cycles (Call et al., 2015) within mangrove systems. Therefore, while our data provides insights into the flux rates and mechanisms driving carbon and greenhouse gas dynamics in Shark River during the study period, long-term seasonal and interannual variability cannot be assessed.

426 In estuarine sediments, TAlk, dissolved carbon and greenhouse gases are known to be 427 driven by redox reactions coupled to remineralisation of organic matter (Burdige, 2011). 428 Compared to freshwater and seawater endmembers, estuarine waters of Shark River were 429 strongly depleted in DO, suggesting high aerobic carbon mineralization rates in the 430 mangrove-dominated area. The relative importance of different metabolic processes of 431 carbon remineralisation can be examined through linear regression of salinity normalized 432 TAlk (TAlk<sub>n</sub>) and salinity normalized DIC (DIC<sub>n</sub>) (Bouillon et al., 2007; Friis et al., 2003). 433 The slopes resulting from TA<sub>n</sub> and DIC<sub>n</sub> regressions are characteristic for the prevailing 434 metabolic process: -0.2 for aerobic respiration, 0.8 for denitrification, 1.0 for sulfate 435 reduction, 2.0 for CaCO<sub>3</sub> dissolution, 4.0 for manganese reduction and 8.0 for iron reduction. 436 The slopes found during the spatial surveys (0.87), the GI (0.64) and SR (0.45) time series 437 suggest a combination of aerobic respiration, denitrification, sulfate reduction and carbonate 438 dissolution were likely most dominant (Figure 7). However, denitrification can be neglected, 439 since due to limited nitrate availability, denitrification rates at Shark River are very low 440 (Inglett et al., 2011), explaining also the low N<sub>2</sub>O emissions observed during this study. 441 Consequently, aerobic respiration, sulfate reduction and carbonate dissolution were the major 442 metabolic pathways driving TAlk, dissolved carbon and greenhouse gas dynamics at Shark 443 River.



444
 445 Figure 7. Salinity normalized alkalinity (TAlk<sub>n</sub>) plotted against salinity normalized dissolved inorganic carbon (DIC<sub>n</sub>) for upstream (GI) and downstream (SR) time series measurements and both spatial surveys (SV).

447 Contributions of metabolic processes strongly differed between the individual 448 measurements. At downstream SR, which had higher DO concentrations, aerobic respiration 449 seemed to play a more dominant role. In contrast, at the upstream site GI and the spatial 450 surveys, sulfate reduction and carbonate dissolution were more important. Since aerobic 451 respiration decouples DIC and TAlk production, TAlk<sub>n</sub> and DIC<sub>n</sub> were not correlated at SR. 452 In contrast, high correlations at GI and during the surveys suggested similar production 453 processes for TAlk and DIC. Combining both time series measurements and the spatial 454 surveys yields an even higher slope (0.93, Figure 8) than the spatial surveys alone, thus highlighting the overall importance of sulfate reduction and carbonate dissolution within the 455 456 estuary.

457 Slopes from TAlk<sub>n</sub> and DIC<sub>n</sub> regressions reported in previous mangrove studies ranged between 0.44 and 0.92 (Bouillon et al., 2007; Ho et al., 2017; Koné & Borges, 2008; 458 459 Sippo et al., 2016; Zablocki et al., 2011). The slope during SR time series was at the lower, 460 and during the spatial surveys at the upper end of the previously described values. The fact 461 that the overall slope, combing all measurements, was slightly higher than reported values is possibly due to the additional TAlk production from carbonate dissolution, since Shark River 462 drains at a large carbonate basin. Based on a  $\delta^{13}$ C mass balance for Shark River, Ho et al. 463 464 (2017) estimated that carbonate dissolution accounted for 34% of the estuarine DIC production. If a similar proportion of carbonate dissolution to DIC production occurred 465 466 during our study, then the proportion of aerobic respiration and sulphate reduction to DIC 467 production would be 34% and 32% respectively (assuming no other major respiration 468 pathways).

469 Being primarily produced within estuarine sediments, TAlk, dissolved carbon and 470 greenhouse gases are largely derived from porewater, which is constantly being exchanged with surface water via tidal pumping (Call et al., 2015; Chen et al., 2018; Maher et al., 471 2013a). During the spatial survey, the natural porewater tracer <sup>222</sup>Rn peaked at the mid 472 473 estuary (Figure 3), indicating increased porewater inputs within the mangrove area. Observed 474 <sup>222</sup>Rn values, which reached up to ~ 10000 dpm/m<sup>3</sup> during the GI time series, were in the 475 midrange compared to values reported previously (Call et al., 2015; Gleeson et al., 2013; 476 Taillardat et al., 2018; Tait et al., 2016), suggesting exchange rates similar to other mangrove 477 systems. Spanning a latitudinal gradient, Tait et al. (2016) reported mangrove porewater exchange rates between 2 and 36 cm/d. High porewater exchange rates in mangroves can be a
result of macropores, such as those from crab burrows, which expose carbon mineralization
products to tidally driven circulation (Stieglitz et al., 2013).

481 Positive correlations between TAlk, dissolved carbon and greenhouse gases with <sup>222</sup>Rn suggest that porewater input was an important driver of carbon cycling at Shark River. 482 Similarly, previous studies reported positive correlations for <sup>222</sup>Rn with TAlk, DIC, DOC, 483 484 CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O in mangroves (Call et al., 2015; Call et al., 2019; Faber et al., 2014; Maher et al., 2013a; Reading et al., 2017; Sadat-Noori et al., 2016; Taillardat et al., 2018). 485 486 Maher et al. (2013a) found that 89-92% of DOC and 93 - 99% of DIC export from a 487 subtropical mangrove creek was driven by porewater input. Results of Call et al. (2015) 488 showed that porewater exchange controlled CO<sub>2</sub> and CH<sub>4</sub> concentrations with exchange rates 489 driven by tidal amplitude changes over spring-neap cycles. Santos et al. (2019) reported significant porewater fluxes of TAlk ( $124 \pm 131 \text{ mmol/m}^2/\text{d}$ ), DIC ( $256 \pm 203 \text{ mmol/m}^2/\text{d}$ ), 490 DOC ( $283 \pm 190 \text{ mmol/m}^2/\text{d}$ ), CO<sub>2</sub> ( $120 \pm 78 \text{ mmol/m}^2/\text{d}$ ) and CH<sub>4</sub> ( $1.2 \pm 0.8 \text{ mmol/m}^2/\text{d}$ ) at 491 492 a subtropical mangrove and saltmarsh dominated creek.

During the present study, correlations between <sup>222</sup>Rn and all studied parameters were 493 much higher ( $r \ge 0.78$ ) for spatial surveys than for individual time series ( $\overline{r} \le 0.80$ ), in part 494 because measured gases, including <sup>222</sup>Rn, followed a hysteresis during the time series (Figure 495 4). Hysteresis for  $^{222}$ Rn, CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O were most probably a result of long equilibration 496 times (30 min for  $^{222}$ Rn and CH<sub>4</sub>, 10 min for CO<sub>2</sub> and N<sub>2</sub>O) causing overlying signals during 497 498 turning tides. Since changes from high to low concentrations require longer equilibration times than low to high transitions (Webb et al., 2016),  $^{222}$ Rn and greenhouse gas peaks during low tide were delayed. As a consequence,  $^{222}$ Rn correlated more with CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O 499 500 during the time series than with dissolved carbon and TAlk, whose analysis do not require 501 502 equilibration and had thus similar concentrations during spatial surveys and time series 503 (Figure 3 and 4). Moreover, having identical equilibration times (30 minutes), <sup>222</sup>Rn and CH<sub>4</sub> 504 correlations were particularly high ( $r \ge 0.7$ ) during the time series compared to all other 505 parameters. An alternative explanation for delayed radon and greenhouse gas peaks during 506 time series include natural processes, such as delayed porewater input (Santos et al., 2019) or 507 different sink processes for dissolved carbon parameters and gases (Sadat-Noori et al., 2016). 508 However, similar trends for dissolved carbon parameters and measured gases during the 509 spatial surveys indicate that methodological reasons are likely responsible for delayed radon 510 and greenhouse gas peaks.

## 511 4.3 Lateral carbon fluxes and greenhouse gas emissions

At Shark River, TAlk, DIC and DOC were produced within the estuary and exported 512 513 to the Gulf of Mexico (Table 1). The two independent methods applied (Lagrangian and 514 Eulerian) were in close agreement, validating the lateral export values and their relative 515 portions. The estuarine carbon export was dominated by DIC (78 - 87%), whereas DOC 516 played only a minor role (13 - 22%). Similarly, previous studies showed that in mangroves 517 most of the dissolved carbon is exported in the form of DIC (Faber et al., 2014; Maher et al., 518 2018; Maher et al., 2013a; Taillardat et al., 2018). Previous work by Ho et al. (2017), found a 519 similar DIC contribution of 82 - 83% of the dissolved carbon fluxes at Shark River.

520 Quantification of mangrove contributions is beyond the scope of this study, but using 521 <sup>13</sup>C budgets previous studies identified mangroves as major estuarine sources for dissolved 522 carbon (Bouillon et al., 2007; Ho et al., 2017; Ray et al., 2018b). Ho et al. (2017) estimated 523 that at Shark River 65% of the estuarine DIC was mangrove-derived with the remainder being carbonate dissolution, since Shark River drains a carbonate basin. Applying this ratio to the estuarine fluxes examined during this study, the mangrove derived DIC flux was ~8.3 x  $10^5$  mol/d while carbonate dissolution contributed ~4.5 x  $10^5$  mol/d.

527 In order to compare lateral export with literature values, fluxes were normalized to the 528 inundated area. Since no high-resolution DEM was available for the study site, the inundated 529 area is associated with large uncertainties, resulting in large uncertainty ranges for the scaled 530 areal rates (Table 1). It has to be noted, that in the present study as well as in the literature, areal rates based on Eulerian approaches were higher than rates based on Lagrangian 531 532 approaches. However, comparing similar methods, estuarine TAlk, DIC and DOC fluxes 533 were consistent with previously published rates at Shark River as well as concordant with 534 exchange rates reported for other mangrove-dominated systems (Table 3).

The Eulerian TAlk export (97 mmol/ $m^2/d$ ) was slightly higher than the average TAlk 535 export rate (76 mmol/m<sup>2</sup>/d, n = 11) of mangrove-dominated sites examined with the Eulerian 536 537 approach (Table 3). The slightly elevated TAlk export at Shark River compared to previous 538 studies might be due to additional TAlk input by carbonate dissolution. The Lagrangian DIC export (80 mmol/m<sup>2</sup>/d) was higher than values reported by Ho et al. (2017) (15 – 20 539 540  $mmol/m^2/d$ ). Comparing continuous DIC measurements from Ho et al. (2017) with data 541 presented here suggests that larger estuarine DIC inputs during our study period were 542 responsible for the higher DIC exports compared to Ho et al. (2017). The Eulerian DIC 543 export (142 mmol/m<sup>2</sup>/d) was close to the global DIC export (159 mmol/m<sup>2</sup>/d) estimated by 544 Bouillon et al. (2008), who suggested that DIC fluxes may be the unaccounted carbon sink in 545 mangroves. Since this publication by Bouillon et al. (2008), a few studies quantified DIC exports from mangroves (149  $\pm$  173 mmol/m<sup>2</sup>/d, n = 15), with an average similar to the 546 547 Eulerian export presented here  $(142 \text{ mmol/m}^2/\text{d})$ .

The Eulerian DOC export (39 mmol/m<sup>2</sup>/d) was very similar to values previously reported for Shark River (41 mmol/m<sup>2</sup>/d) using a similar method (Bergamaschi et al., 2012), and marginally higher than the global average (34 mmol/m<sup>2</sup>/d) (Bouillon et al., 2008). Lagrangian DOC export (12 mmol/m<sup>2</sup>/d) was slightly higher than other Lagrangian export rates (2 mmol/m<sup>2</sup>/d) at this site (Ho et al., 2017) and nearly identical to DOC export rates (13 mmol/m<sup>2</sup>/d) analysed with flumes within the Shark River mangroves (Romigh et al., 2006).

554 The high agreement between observed TAlk, DIC and DOC export rates and other 555 values reported in the literature using the same methodological approach, highlights the importance of the method choice. The method choice might have a higher impact on export 556 557 rates than on differences between seasons, which appear to have little effect on DIC export rates in Shark River (Volta et al., 2018). Analysing fluxes at Gunboat Island (GI) for an entire 558 year, Volta et al. (2018) found that DIC (23.2 -  $25.4 \times 10^5$  mol/d) and CO<sub>2</sub> emissions (5.5 -559  $7.8 \times 10^5$  mol/d) varied little between seasons. Thus, even though this study was limited to a 560 561 short period, the fluxes might still be representative for this site.

Shark River was a source of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O to the atmosphere. The air-water flux 562 of  $CO_2$  (92 mmol/m<sup>2</sup>/d) was close to previously measured emissions at this site (Ho et al., 563 2017), and was higher than the global average for mangrove systems (60 mmol/ $m^2/d$ ) 564 565 (Bouillon et al., 2008). High CO<sub>2</sub> emissions at Shark River are driven by upstream DIC input originating from freshwater marshes (Ho et al., 2017). In contrast to CO<sub>2</sub>, CH<sub>4</sub> (60 566  $\mu$ mol/m<sup>2</sup>/d) and N<sub>2</sub>O emissions (2  $\mu$ mol/m<sup>2</sup>/d) were much lower than the global average for 567 568 mangroves (Murray et al., 2015; Rosentreter et al., 2018b). Air-water fluxes of  $CH_4$  were 569 possibly reduced by increased CH<sub>4</sub> oxidation within the water column as a result of oxygen 570 rich fresh and saltwater input, compared to more oxygen limited waters such as tidal creeks.

- 571 Low N<sub>2</sub>O emissions might be due to nitrate limitation within the mangrove area (Inglett et al.,
- 572 2011). Other pristine mangrove systems, which are naturally low in nitrogen, were found to
- have minimal  $N_2O$  emissions (Reading et al., 2017) and even  $N_2O$  undersaturation (Maher et
- 574 al., 2016).

Confidential manuscript submitted to Journal of Geophysical Research: Biogeosciences

575	Table 3: Literature values for lateral dissolved carbon and alkalinity ex	xchange (scaled to the inu	ndated mangrove area) a	as well as greenhouse gas emissions	•

Reference	Country	Site	TAlk exchange (mmol/m²/d)	DIC exchange (mmol/m²/d)	DOC exchange (mmol/m²/d)	CO <sub>2</sub> exchange (mmol/m <sup>2</sup> /d)	CH4 exchange (µmol/m²/d)	N <sub>2</sub> O exchange (µmol/m²/d)
This study	LIC A	Shork Divor	97 (48 - 193) <sup>e</sup>	142 (71 - 284) <sup>e</sup>	39 (20 - 79) <sup>e</sup>			
This study	USA	SHAIK KIVEI	64 (32 - 128) <sup>1</sup>	80 (40 - 161) <sup>1</sup>	$12(4-24)^{1}$	92	60	2
Ho et al. (2017) and		Shark River (dry 1)		$21 \pm 12^1$	$2\pm1^1$	$105 \pm 9$		
Ho et al. (2014)	USA	Shark River (dry 2)		$13 \pm 14^1$	$2\pm4^{1}$	$99 \pm 6$		
Bergamaschi et al. (2012)	USA	Shark River			$41 \pm 3^{e}$			
Romigh et al. (2006)	USA	Shark River			13 <sup>f</sup>			
$\mathbf{M}_{1}$	A	Moreton Bay (summer)		183 <sup>e</sup>	41 <sup>e</sup>			
Maner et al. (2013a)	Australia	Moreton Bay (winter)		340 <sup>e</sup>	12 <sup>e</sup>			
Educated (2014)	A	Western Port (WI)	310 <sup>e</sup>	450 <sup>e</sup>	25 <sup>e</sup>	17		
Faber et al. (2014)	Australia	Western Port (CI)	$46^{\rm e}$	130 <sup>e</sup>	$0^{e}$	19		
		Darwin	116 <sup>e</sup>	85 <sup>e</sup>		40		$-0.1 \pm 0.01$
		Hinchinbrook Island	21 <sup>e</sup>	22 <sup>e</sup>		30		- 3 ± 0.06
Sippo et al. (2016) and	Australia	Seventeen Seventy	81 <sup>e</sup>	-97 <sup>e</sup>		10		$-2 \pm 0.1$
Maher et al. (2016)		Jacobs Well	12 <sup>e</sup>	83 <sup>e</sup>		19		- 3 ± 0.08
		Newcastle	116 <sup>e</sup>	77 <sup>e</sup>		46		$0.7\pm0.03$
		Barwon Heads	-1 <sup>e</sup>	-3 <sup>e</sup>		9		$-1 \pm 0.07$
Sadat-Noori et al. (2016)	Australia	Korogoro Creek	$23\pm5^{ec}$	$20 \pm 4^{e c}$	$9\pm2^{e\ c}$	869	26000	
Maher et al. (2018)	Australia	Moreton Bay	$96 \pm 35^{e}$	$212\pm74^{e}$	$59\pm22^{e}$	23 - 42	33 - 54	
Santos et al. (2019)	Australia	Evans Head	$12 \pm 6^{e\ c}$	$12 \pm 6^{e\ c}$	$2 \pm 2^{e\ c}$	$63 \pm 166$	$270\pm30$	
Ray et al. (2018a)	India	Sundarbans		202 <sup>e</sup>	162 <sup>e</sup>			
Taillardat et al. (2018)	Vietnam	Can Gio		352 - 678 <sup>e</sup>	21 - 68 <sup>e</sup>	70 - 174		
Bouillon et al. (2008)	global			$159\pm120$	$34 \pm 14$	$60 \pm 45$		
Rosentreter et al. (2018b)	global						$288\pm73$	
Murray et al. (2015)	global							22 (2-144)

Note: Method: <sup>e</sup>Eulerian approach, <sup>l</sup>Lagrangian approach, <sup>f</sup>Flumes, <sup>e</sup>scaled to the catchment area

577 The Shark River estuary was a net source of TAlk and dissolved carbon to the coastal 578 ocean and a source of greenhouse gases to the atmosphere (Figure 8). Most of the inorganic carbon was exported laterally (83 - 93%), mainly as DIC, whereas only a small share was 579 emitted to the atmosphere as CO<sub>2</sub> and CH<sub>4</sub>. Carbon burial rates (123  $\pm$  19 g C/m<sup>2</sup>/y) of the 580 mangrove forest surrounding Shark River (Breithaupt et al., 2014) are two to four times lower 581 than lateral DIC export  $(255 - 452 \text{ g C/m}^2/\text{y})$  presented here, emphasising the importance of 582 583 considering lateral carbon export in blue carbon budgets. Upscaling all available TAlk and 584 DIC export rates (Table 3) to the global mangrove area (Giri et al., 2011) suggests a global TAlk export of 4.8 Tmol/y and a DIC export of 146 Tg C/y, which is an order of magnitude 585 586 higher than the global burial rate of  $\sim 26$  Tg C/y estimated by Breithaupt et al. (2012). Both 587 export rates are higher than previous global estimates for DIC ( $43 \pm 12$  Tg C/y) and TAlk (4.2 Tmol/y) export, which were limited to six Australian mangrove creeks (Sippo et al., 588 589 2016). However, the global estimates presented here are still based on a relatively small 590 number of studies, and more research is clearly required to validate global export rates. This is especially the case in the low latitude tropics  $(0-5^{\circ})$  where most mangroves occur, but the 591 592 number of estimates of TAlk and DIC export rates are very limited.



593 594

Figure 8. Alkalinity, dissolved carbon and greenhouse gas fluxes at the Shark River estuary are presented in 595 mol/d (a). The estuarine carbon budget is presented in Gg C/y (b). Values for particulate organic carbon (POC) 596 were retrieved from He et al. (2014), carbon burial from Breithaupt et al. (2014) and DIC, DOC and CO<sub>2</sub> fluxes 597 were examined during the present study (b).

#### 598 **5 Conclusion**

599 By combining spatial surveys and time series approaches at the mangrove-dominated 600 Shark River, we found that the estuary was a source for alkalinity and dissolved carbon to the 601 Gulf of Mexico, and a source of greenhouse gas emissions to the atmosphere. The dominant metabolic process changed along the estuary, from anaerobic processes in the upper estuary 602 603 to a greater dominance of aerobic metabolism in the lower estuary. Additional to carbon 604 remineralization, carbonate dissolution and porewater inputs were identified as important 605 drivers controlling carbon fluxes. Lateral DIC export exceeds mangrove sedimentary carbon 606 burial rates by at least twofold, resulting in an underestimation of the net carbon sequestration 607 effect of mangroves. The majority of the exported DIC was carbonate alkalinity, which may 608 buffer acidification of coastal waters. The climate change mitigation provided by the 609 mangrove-dominated estuary was partly offset by CH<sub>4</sub> and N<sub>2</sub>O emissions. However, 610 greenhouse gas emissions were minor compared to carbon sequestration and alkalinity 611 export. To accurately assess the capacity of OAlk to buffer coastal acidification, future 612 studies should quantitatively account for OAlk in the TAlk pool, and characterise the organic 613 compounds contributing to the OAlk pool. Furthermore, DOC and fDOM seem to be 614 promising OAlk proxies, which may provide a less laborious option for quantifying OAlk. 615 For researchers examining alkalinity, dissolved carbon and greenhouse gas dynamics in 616 estuaries, it is recommended to combine both spatial and temporal approaches to provide independent estimates of fluxes and enhanced cross validation. We argue that accounting for 617 618 lateral alkalinity and dissolved carbon export, as well as greenhouse gas fluxes, is crucial to 619 evaluate the potential of mangroves to mitigate climate change. We therefore urge the 620 scientific community to work towards integrating these processes into blue carbon budgets.

#### 621 Literature

- Atwood, T. B., R. M. Connolly, H. Almahasheer, P. E. Carnell, C. M. Duarte, C. J. E. Lewis, et al. (2017).
  Global patterns in mangrove soil carbon stocks and losses. *Nature Climate Change*, 7(7), 523, doi:10.1038/NCLIMATE3326
- Baker, A., and R. G. Spencer (2004). Characterization of dissolved organic matter from source to sea using
  fluorescence and absorbance spectroscopy. *Science of the Total Environment*, 333(1-3), 217-232,
  doi:10.1016/j.scitotenv.2004.04.013
- Barr, J. G., V. Engel, J. D. Fuentes, J. C. Zieman, T. L. O'Halloran, T. J. Smith III, and G. H. Anderson (2010).
   Controls on mangrove forest-atmosphere carbon dioxide exchanges in western Everglades National
   Park. *Journal of Geophysical Research*, *115*(G2), G02020, doi:10.1029/2009JG001186
- Benson, B. B., and D. Krause (1984). The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere. *Limnology and Oceanography*, 29(3), 620-632, doi:10.4319/lo.1984.29.3.0620
- Bergamaschi, B. A., D. P. Krabbenhoft, G. R. Aiken, E. Patino, D. G. Rumbold, and W. H. Orem (2012).
  Tidally driven export of dissolved organic carbon, total mercury, and methylmercury from a mangrovedominated estuary. *Environmental Science & Technology*, 46(3), 1371-1378, doi:10.1021/es2029137
- Bouillon, S., A. V. Borges, E. Castañeda-Moya, K. Diele, T. Dittmar, N. C. Duke, et al. (2008). Mangrove
  production and carbon sinks: a revision of global budget estimates. *Global Biogeochemical Cycles*,
  22(2), GB2013, doi:10.1029/2007GB003052
- Bouillon, S., F. Dehairs, B. Velimirov, G. Abril, and A. V. Borges (2007). Dynamics of organic and inorganic
   carbon across contiguous mangrove and seagrass systems (Gazi Bay, Kenya). *Journal of Geophysical Research*, *112*(G2), G02018, doi:10.1029/2006JG000325
- Breithaupt, J. L., J. M. Smoak, T. J. Smith III, and C. J. Sanders (2014). Temporal variability of carbon and nutrient burial, sediment accretion, and mass accumulation over the past century in a carbonate platform mangrove forest of the Florida Everglades. *Journal of Geophysical Research: Biogeosciences*, *119*(10), 2032-2048, doi:10.1002/2014JG002715
- Breithaupt, J. L., J. M. Smoak, T. J. Smith III, C. J. Sanders, and A. Hoare (2012). Organic carbon burial rates in mangrove sediments: Strengthening the global budget. *Global Biogeochemical Cycles*, 26(3), GB3011, doi:10.1029/2012GB004375
- Burdige, D. (2011). Estuarine and coastal sediments-coupled biogeochemical cycling. *Treatise on Estuarine* and Coastal Science, 5, 279-308, doi:10.1002/2015GB005324
- Burnett, W., G. Kim, and D. Lane-Smith (2001). A continuous monitor for assessment of <sup>222</sup>Rn in the coastal
  ocean. Journal of Radioanalytical and Nuclear Chemistry, 249(1), 167-172,
  doi:10.1023/A:1013217821419
- Cai, W.-J., Y. Wang, and R. E. Hodson (1998). Acid-base properties of dissolved organic matter in the estuarine
   waters of Georgia, USA. *Geochimica et Cosmochimica Acta*, 62(3), 473-483, doi:10.1016/S0016 7037(97)00363-3
- Call, M., D. T. Maher, I. R. Santos, S. Ruiz-Halpern, P. Mangion, C. J. Sanders, et al. (2015). Spatial and temporal variability of carbon dioxide and methane fluxes over semi-diurnal and spring–neap–spring timescales in a mangrove creek. *Geochimica et Cosmochimica Acta*, 150, 211-225, doi:10.1016/j.gca.2014.11.023
- Call, M., I. R. Santos, T. Dittmar, C. E. de Rezende, N. E. Asp, and D. T. Maher (2019). High pore-water derived CO<sub>2</sub> and CH<sub>4</sub> emissions from a macro-tidal mangrove creek in the Amazon region. *Geochimica et Cosmochimica Acta*, 247, 106-120, doi:10.1016/j.gca.2018.12.029
- 665 Chen, R., and R. R. Twilley (1999). Patterns of mangrove forest structure and soil nutrient dynamics along the
   666 Shark River Estuary, Florida. *Estuaries*, 22(4), 955-970, doi:10.2307/1353075
- 667 Chen, X., F. Zhang, Y. Lao, X. Wang, J. Du, and I. R. Santos (2018). Submarine groundwater discharge-derived
   668 carbon fluxes in mangroves: An important component of blue carbon budgets? *Journal of Geophysical* 669 *Research: Oceans*, 123(9), 6962-6979, doi:10.1029/2018JC014448
- 670 Dickson, A. G. (2010). Standards for ocean measurements. *Oceanography*, 23(3), 34-47, doi:10.5670/oceanog.2010.22
- Donato, D. C., J. B. Kauffman, D. Murdiyarso, S. Kurnianto, M. Stidham, and M. Kanninen (2011). Mangroves
  among the most carbon-rich forests in the tropics. *Nature geoscience*, 4(5), 293, doi:10.1038/NGEO1123
- Emerson, S., and J. Hedges (2008). Chemical oceanography and the marine carbon cycle. *Cambridge University Press*, doi:10.1017/CBO9780511793202
- Faber, P. A., V. Evrard, R. J. Woodland, I. C. Cartwright, and P. L. Cook (2014). Pore-water exchange driven
  by tidal pumping causes alkalinity export in two intertidal inlets. *Limnology and Oceanography*, 59(5),
  1749-1763, doi:10.4319/lo.2014.59.5.1749

- Fong, M. B., and A. G. Dickson (2019). Insights from GO-SHIP hydrography data into the thermodynamic consistency of CO<sub>2</sub> system measurements in seawater. *Marine Chemistry*, 211, 52-63, doi:10.1016/j.marchem.2019.03.006
- Friederich, G., P. Walz, M. Burczynski, and F. Chavez (2002). Inorganic carbon in the central California
  upwelling system during the 1997–1999 El Niño–La Niña event. *Progress in Oceanography*, 54(1-4),
  185-203, doi:10.1016/S0079-6611(02)00049-6.
- Friesen, S. D., C. Dunn, and C. Freeman (2018). Decomposition as a regulator of carbon accretion in mangroves: a review. *Ecological Engineering*, *114*, 173-178, doi:10.1016/j.ecoleng.2017.06.069
- Friis, K., A. Körtzinger, and D. W. Wallace (2003). The salinity normalization of marine inorganic carbon
   chemistry data. *Geophysical Research Letters*, 30(2), 1085, doi:10.1029/2002GL015898
- 690 Giri, C., E. Ochieng, L. L. Tieszen, Z. Zhu, A. Singh, T. Loveland, et al. (2011). Status and distribution of
   691 mangrove forests of the world using earth observation satellite data. *Global Ecology and* 692 *Biogeography*, 20(1), 154-159, doi:10.1111/j.1466-8238.2010.00584.x
- 693 Gleeson, J., I. R. Santos, D. T. Maher, and L. Golsby-Smith (2013). Groundwater–surface water exchange in a mangrove tidal creek: evidence from natural geochemical tracers and implications for nutrient budgets.
   695 Marine Chemistry, 156, 27-37, doi:10.1016/j.marchem.2013.02.001
- Hammer, K., B. Schneider, K. Kuliński, and D. E. Schulz-Bull (2017). Acid-base properties of Baltic Sea dissolved organic matter. *Journal of Marine Systems*, 173, 114-121, doi:10.1016/j.jmarsys.2017.04.007
- He, D., R. N. Mead, L. Belicka, O. Pisani, and R. Jaffé (2014). Assessing source contributions to particulate
  organic matter in a subtropical estuary: A biomarker approach. *Organic Geochemistry*, 75, 129-139,
  doi:10.1016/j.orggeochem.2014.06.012
- Hernández-Ayon, M. J., A. Alberto, A. Dickson, T. Camiro-Vargas, and E. Valenzuela-Espinoza (2007).
   Estimating the contribution of organic bases from microalgae to the titration alkalinity in coastal seawaters. *Limnology and Oceanography: Methods*, 5(7), 225-232, doi:10.4319/lom.2007.5.225
   Ho, D. T., N. Coffineau, B. Hickman, N. Chow, T. Koffman, and P. Schlosser (2016). Influence of current
  - Ho, D. T., N. Coffineau, B. Hickman, N. Chow, T. Koffman, and P. Schlosser (2016). Influence of current velocity and wind speed on air-water gas exchange in a mangrove estuary. *Geophysical Research Letters*, 43(8), 3813-3821, doi:10.1002/2016GL068727

705

706

707

708

709

- Ho, D. T., S. Ferrón, V. C. Engel, W. T. Anderson, P. K. Swart, R. M. Price, and L. Barbero (2017). Dissolved carbon biogeochemistry and export in mangrove-dominated rivers of the Florida Everglades. *Biogeosciences*, 14(9), 2543-2559, doi:10.5194/bg-14-2543-2017
- Ho, D. T., S. Ferrón, V. C. Engel, L. G. Larsen, and J. G. Barr (2014). Air-water gas exchange and CO<sub>2</sub> flux in a mangrove-dominated estuary. *Geophysical Research Letters*, 41(1), 108-113, doi:10.1002/2013GL058785
- Hu, X. (2020). Effect of Organic Alkalinity on Seawater Buffer Capacity: A Numerical Exploration. Aquatic Geochemistry, doi:10.1007/s10498-020-09375-x
- Hunt, C., J. Salisbury, and D. Vandemark (2011). Contribution of non-carbonate anions to total alkalinity and overestimation of pCO<sub>2</sub> in New England and New Brunswick rivers. *Biogeosciences*, 8(10), 3069-3076, doi:10.5194/bg-8-3069-2011
- Inglett, P., V. Rivera-Monroy, and J. Wozniak (2011). Biogeochemistry of nitrogen across the Everglades
   landscape. *Critical Reviews in Environmental Science and Technology*, 41(S1), 187-216,
   doi:10.1080/10643389.2010.530933
- Fight Provide the set of the se
- Kaul, L. W., and P. N. Froelich (1984). Modeling estuarine nutrient geochemistry in a simple system. *Geochimica et Cosmochimica Acta*, 48(7), 1417-1433, doi:10.1016/0016-7037(84)90399-5
  Kim, H. C., and K. Lee (2009). Significant contribution of dissolved organic matter to seawater alkalinity.
- Kim, H. C., and K. Lee (2009). Significant contribution of dissolved organic matter to seawater alkalinity.
   *Geophysical Research Letters*, 36(20), L20603, doi:10.1029/2009GL040271
- Ko, Y. H., K. Lee, K. H. Eom, and I. S. Han (2016). Organic alkalinity produced by phytoplankton and its effect
   on the computation of ocean carbon parameters. *Limnology and Oceanography*, 61(4), 1462-1471,
   doi:10.1002/lno.10309
- Koeve, W., and A. Oschlies (2012). Potential impact of DOM accumulation on fCO<sub>2</sub> and carbonate ion computations in ocean acidification experiments. *Biogeosciences*, 9(10), 3787-3798, doi:10.5194/bg-9-3787-2012
- Koné, Y.-M., and A. Borges (2008). Dissolved inorganic carbon dynamics in the waters surrounding forested
   mangroves of the Ca Mau Province (Vietnam). *Estuarine, Coastal and Shelf Science*, 77(3), 409-421,
   doi:10.1016/j.ecss.2007.10.001
- Kuliński, K., B. Schneider, K. Hammer, U. Machulik, and D. Schulz-Bull (2014). The influence of dissolved organic matter on the acid–base system of the Baltic Sea. *Journal of Marine Systems*, *132*, 106-115, doi:10.1016/j.jmarsys.2014.01.011

- Lewis, E., and D. Wallace (1998). Program developed for CO<sub>2</sub> system calculations, carbon dioxide information
   analysis center. *Oak Ridge National Laboratory, US Department of Energy*, doi:10.2172/639712
- Lukawska-Matuszewska, K., W. Grzybowski, A. Szewczun, and P. Tarasiewicz (2018). Constituents of organic
  alkalinity in pore water of marine sediments. *Marine Chemistry*, 200, 22-32,
  doi:10.1016/j.marchem.2018.01.012
- Maher, D. T., M. Call, I. R. Santos, and C. J. Sanders (2018). Beyond burial: Lateral exchange is a significant
   atmospheric carbon sink in mangrove forests. *Biology Letters*, 14(7), 20180200,
   doi:10.1098/rsbl.2018.0200
- Maher, D. T., and B. D. Eyre (2010). Benthic fluxes of dissolved organic carbon in three temperate Australian
   estuaries: Implications for global estimates of benthic DOC fluxes. *Journal of Geophysical Research: Biogeosciences*, *115*(G4), doi:10.1029/2010JG001433
- Maher, D. T., and B. D. Eyre (2012). Carbon budgets for three autotrophic Australian estuaries: Implications for global estimates of the coastal air-water CO<sub>2</sub> flux. *Global Biogeochemical Cycles*, 26(1), GB1032, doi:10.1029/2011GB004075
- Maher, D. T., I. R. Santos, L. Golsby-Smith, J. Gleeson, and B. D. Eyre (2013a). Groundwater-derived dissolved inorganic and organic carbon exports from a mangrove tidal creek: The missing mangrove carbon sink? *Limnology and Oceanography*, 58(2), 475-488, doi:10.4319/lo.2013.58.2.0475
- Maher, D. T., I. R. Santos, J. R. Leuven, J. M. Oakes, D. V. Erler, M. C. Carvalho, and B. D. Eyre (2013b).
   Novel use of cavity ring-down spectroscopy to investigate aquatic carbon cycling from microbial to ecosystem scales. *Environmental Science & Technology*, 47(22), 12938-12945, doi:10.1021/es4027776
- Maher, D. T., J. Z. Sippo, D. R. Tait, C. Holloway, and I. R. Santos (2016). Pristine mangrove creek waters are a sink of nitrous oxide. *Scientific Reports*, 6, 25701, doi:10.1038/srep25701
- Martz, T. R., J. G. Connery, and K. S. Johnson (2010). Testing the Honeywell Durafet<sup>®</sup> for seawater pH applications. *Limnology and Oceanography: Methods*, 8(5), 172-184, doi:10.4319/lom.2010.8.172
- Millero, F. J. (2010). Carbonate constants for estuarine waters. *Marine and Freshwater Research*, 61(2), 139-142, doi:10.1071/MF09254
- Moran, M. A., W. M. Sheldon, and R. G. Zepp (2000). Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter. *Limnology and Oceanography*, 45(6), 1254-1264, doi:10.4319/lo.2000.45.6.1254
- Murray, R. H., D. V. Erler, and B. D. Eyre (2015). Nitrous oxide fluxes in estuarine environments: response to global change. *Global Change Biology*, 21(9), 3219-3245, doi:10.1111/gcb.12923
- Olmsted, I. C., and T. V. Armentano (1997). Vegetation of Shark Slough, Everglades National Park, South
   Florida Natural Resources Center, Everglades National Park Homestead, FL.
- 772 Petuch, E. J., and C. Roberts (2007). *The geology of the Everglades and adjacent areas*, CRC Press.
- Pierrot, D., C. Neill, K. Sullivan, R. Castle, R. Wanninkhof, H. Lüger, et al. (2009). Recommendations for
   autonomous underway pCO<sub>2</sub> measuring systems and data-reduction routines. *Deep Sea Research Part II*, 56(8-10), 512-522, doi:10.1016/j.dsr2.2008.12.005
- Ray, R., A. Baum, T. Rixen, G. Gleixner, and T. Jana (2018a). Exportation of dissolved (inorganic and organic)
  and particulate carbon from mangroves and its implication to the carbon budget in the Indian
  Sundarbans. Science of the Total Environment, 621, 535-547,
  doi:doi.org/10.1016/j.scitotenv.2017.11.225
- Ray, R., E. Michaud, R. Aller, V. Vantrepotte, G. Gleixner, R. Walcker, et al. (2018b). The sources and distribution of carbon (DOC, POC, DIC) in a mangrove dominated estuary (French Guiana, South America). *Biogeochemistry*, 138(3), 297-321, doi:10.1007/s10533-018-0447-9
- Reading, M. J., I. R. Santos, D. T. Maher, L. C. Jeffrey, and D. R. Tait (2017). Shifting nitrous oxide source/sink behaviour in a subtropical estuary revealed by automated time series observations. *Estuarine, Coastal and Shelf Science, 194*, 66-76, doi:10.1016/j.ecss.2017.05.017
- Romigh, M. M., S. E. Davis, V. H. Rivera-Monroy, and R. R. Twilley (2006). Flux of organic carbon in a riverine mangrove wetland in the Florida Coastal Everglades. *Hydrobiologia*, 569(1), 505-516, doi:10.1007/s10750-006-0152-x
- Rosentreter, J. A., D. Maher, D. Erler, R. Murray, and B. Eyre (2018a). Seasonal and temporal CO<sub>2</sub> dynamics in three tropical mangrove creeks–A revision of global mangrove CO<sub>2</sub> emissions. *Geochimica et Cosmochimica Acta*, 222, 729-745, doi:10.1016/j.gca.2017.11.026
- Rosentreter, J. A., D. T. Maher, D. V. Erler, R. H. Murray, and B. D. Eyre (2018b). Methane emissions partially
  offset "blue carbon" burial in mangroves. *Science Advances*, 4(6), eaao4985,
  doi:10.1126/sciadv.aao4985
- Sadat-Noori, M., D. T. Maher, and I. R. Santos (2016). Groundwater discharge as a source of dissolved carbon
   and greenhouse gases in a subtropical estuary. *Estuaries and Coasts*, 39(3), 639-656,
   doi:10.1007/s12237-015-0042-4

- Santos, I. R., D. T. Maher, and B. D. Eyre (2012). Coupling automated radon and carbon dioxide measurements in coastal waters. *Environmental Science & Technology*, 46(14), 7685-7691, doi:10.1021/es301961b
- Santos, I. R., D. T. Maher, R. Larkin, J. R. Webb, and C. J. Sanders (2019). Carbon outwelling and outgassing
   vs. burial in an estuarine tidal creek surrounded by mangrove and saltmarsh wetlands. *Limnology and Oceanography*, 64(3), 996-1013, doi:10.1002/lno.11090
- Sholkovitz, E., E. Boyle, and N. Price (1978). The removal of dissolved humic acids and iron during estuarine mixing. *Earth and Planetary Science Letters*, 40(1), 130-136, doi:10.1016/0012-821X(78)90082-1
- Sippo, J. Z., D. T. Maher, D. R. Tait, C. Holloway, and I. R. Santos (2016). Are mangroves drivers or buffers of coastal acidification? Insights from alkalinity and dissolved inorganic carbon export estimates across a latitudinal transect. *Global Biogeochemical Cycles*, *30*(5), 753-766, doi:10.1002/2015gb005324
- Stieglitz, T. C., J. F. Clark, and G. J. Hancock (2013). The mangrove pump: the tidal flushing of animal burrows in a tropical mangrove forest determined from radionuclide budgets. *Geochimica et Cosmochimica Acta*, *102*, 12-22, doi:10.1016/j.gca.2012.10.033
- Suryaputra, I. G., I. R. Santos, M. Huettel, W. Burnett, and T. Dittmar (2015). Non-conservative behavior of
   fluorescent dissolved organic matter (FDOM) within a subterranean estuary. *Continental Shelf Research*, 110, 183-190, doi:10.1016/j.csr.2015.10.011
- Taillardat, P., P. Willemsen, C. Marchand, D. Friess, D. Widory, P. Baudron, et al. (2018). Assessing the contribution of porewater discharge in carbon export and CO<sub>2</sub> evasion in a mangrove tidal creek (Can Gio, Vietnam). *Journal of Hydrology*, *563*, 303–318, doi:10.1016/j.jhydrol.2018.05.042
- Tait, D. R., D. T. Maher, P. A. Macklin, and I. R. Santos (2016). Mangrove pore water exchange across a latitudinal gradient. *Geophysical Research Letters*, 43(7), 3334-3341, doi:10.1002/2016GL068289
- Tishchenko, P. Y., K. Wallmann, N. Vasilevskaya, T. Volkova, V. Zvalinskii, N. Khodorenko, and E.
   Shkirnikova (2006). The contribution of organic matter to the alkaline reserve of natural waters.
   *Oceanology*, 46(2), 192-199, doi:10.1134/S0001437006020068
- 822 U.S. Geological Survey (2018), National Water Information System data available on the World Wide Web 823 (USGS Water Data for the Nation), accessed 13 August 2019, at URL: 824 https://waterdata.usgs.gov/nwis/uv, edited.
- Ulfsbo, A., K. Kuliński, L. G. Anderson, and D. R. Turner (2015). Modelling organic alkalinity in the Baltic Sea
   using a Humic-Pitzer approach. *Marine Chemistry*, 168, 18-26, doi:10.1016/j.marchem.2014.10.013
- Volta, C., D. T. Ho, G. Friederich, V. C. Engel, and M. Bhat (2018). Influence of water management and natural variability on dissolved inorganic carbon dynamics in a mangrove-dominated estuary. *Science of the Total Environment*, 635, 479-486, doi:10.1016/j.scitotenv.2018.04.088
- Wanninkhof, R. (2014). Relationship between wind speed and gas exchange over the ocean revisited. *Limnology and Oceanography: Methods*, 12(6), 351-362, doi:10.4319/lom.2014.12.351
- 832 Webb, J. R., D. T. Maher, and I. R. Santos (2016). Automated, in situ measurements of dissolved CO<sub>-2</sub>, CH<sub>4</sub>, 833 and  $\delta^{13}$ C values using cavity enhanced laser absorption spectrometry: Comparing response times of air-834 water equilibrators. *Limnology and Oceanography: Methods*, 14(5), 323-337, doi:10.1002/lom3.10092
- Weiss, R., and B. Price (1980). Nitrous oxide solubility in water and seawater. *Marine Chemistry*, 8(4), 347-359, doi:10.1016/0304-4203(80)90024-9
- Weiss, R. F. (1974). Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Marine Chemistry*, 2(3), 203-215, doi:10.1016/0304-4203(74)90015-2
- Wiesenburg, D. A., and N. L. Guinasso Jr (1979). Equilibrium solubilities of methane, carbon monoxide, and
  hydrogen in water and sea water. *Journal of Chemical and Engineering Data*, 24(4), 356-360,
  doi:10.1021/je60083a006
- Yang, B., R. H. Byrne, and M. Lindemuth (2015). Contributions of organic alkalinity to total alkalinity in coastal waters: A spectrophotometric approach. *Marine Chemistry*, 176, 199-207, doi:10.1016/j.marchem.2015.09.008
- Zablocki, J. A., A. J. Andersson, and N. R. Bates (2011). Diel aquatic CO<sub>2</sub> system dynamics of a Bermudian mangrove environment. *Aquatic Geochemistry*, *17*(6), 841, doi:10.1007/s10498-011-9142-3

847

#### 848 Acknowledgments, Samples, and Data

849 This research project was funded by the Australian Research Council (DP180101285)

and the National Aeronautics and Space Administration (NNX14AJ92G) under the Carbon

851 Cycle Program. We are particularly grateful to Benjamin Hickman for the technical support852 during the fieldtrip and the data analysis. We also like to thank James Ash for supporting us

in the field, as well as Matheus Carvalho de Carvalho for conducting the DOC measurements.

854 The authors declare that there is no conflict of interest. Datasets for this research are available

855 on the PANGAEA database (<u>https://issues.pangaea.de/browse/PDI-23888</u>).